

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Refining of Hydrocarbon Distillates

We, PHILLIPS PETROLEUM COMPANY, a Corporation organized under the laws of the State of Delaware, United States of America, of Bartlesville, State of Oklahoma, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process of treatment of hydrocarbon distillates to prepare blending stocks suitable for aviation fuel purposes. More specifically, it is concerned with a treating process leading to the concomitant reduction of the sulphur and unsaturated hydrocarbon content of gasoline range hydrocarbon distillates.

In the manufacture of high quality aviation fuels, factors of primary importance include: 1—C octane rating U.S. Army-Navy Aeronautical Specification (AN—VV—F—746), 3—C rich-mixture rating U.S. Army-Navy Aeronautical Specification (AN—VV—F—748a) and storage stability. In order to realize large volume production of aviation fuel of requisite 1—C and 3—C ratings it has been necessary to resort to the use of catalytically and thermally cracked distillates because of their relatively high initial octane ratings. Certain types of catalytically produced gasolines are of exceptional value because of their content of aromatic hydrocarbons and their attendant beneficial effect on the 3—C rich-mixture rating. Cracked distillates, in general, and the highly desirable aromatics-containing catalytically cracked distillates, in particular, are known to contain substantial quantities of unsaturated hydrocarbons. It is common practice to increase the octane number of a gasoline by adding to it small amounts of tetraethyl lead. The amount of increase in the octane number of a gasoline which is obtained upon the addition of any specific amount of tetraethyl lead is

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dependent upon the type of hydrocarbons in the gasoline. Thus, if one c.c. of tetraethyl lead fluid is added to a gasoline consisting of paraffinic hydrocarbons, the resulting octane number of the leaded gasoline will be much higher than will the octane number of an olefinic gasoline to which the same quantity of tetraethyl lead has been added and which, prior to addition of tetraethyl lead, had the same octane number as the paraffinic gasoline. Such an increase in octane number is commonly referred to as "tetraethyl lead response" and in the foregoing illustrations, the paraffinic gasoline has a greater tetraethyl lead response, and the olefinic gasoline has a lesser lead response. Because of the adverse lead response of unsaturated distillates, their inclusion in aviation fuels is ordinarily not practiced. Furthermore any appreciable amount of unsaturation may often lead to storage difficulties. Another important factor in meeting quality specifications is the sulphur content of the gasoline, since it is also well known that the presence of sulphur interferes with lead response.

The removal of deleterious unsaturated hydrocarbons and sulphur compounds from cracked gasoline distillates is of recognized value in the preparation of aviation gasoline. Conventional clay treatment is useful in removing diolefinic hydrocarbons; however, the sulphur and olefin content of the distillate is not appreciably affected. Sulphuric acid treatment, if sufficiently severe, will substantially reduce both sulphur and olefin content of hydrocarbons, but has the disadvantages inherent in any acid treating process, combined with the additional undesirable loss of valuable aromatic constituents. Hydrogenation is an obvious expedient for the reduction of both unsaturation and sulphur; however, the net effect of such treatment is a decrease in octane rating due to the formation of low-quality paraffinic hydrocarbons.

Further severe cracking has been recommended in some instances for the reduction of unsaturation, but at best this type of treatment necessarily results in a waste of feed stock through the formation of fixed gases and often fails to reduce the unsaturation to an acceptably low level. Various processes employing adsorbent catalyst have been proposed for the reduction in olefin content of hydrocarbon distillates; however, in general, conditions suitable for polymerization of olefins do not ordinarily have much effect on the sulphur content and in many instances may function to concentrate sulphur in the finished product.

We have found that it is possible simultaneously to reduce both the olefin and sulphur content of gasoline range hydrocarbon distillates by subjecting distillates to treatment over a silica-alumina catalyst under relatively mild reaction conditions, and particularly over a catalyst of this type prepared in a particular way and having a specific composition. We have further found that a wide variety of distillates are responsive to treatment over the present catalyst with a reduction of unsaturation and sulphur content to values substantially less than 50 per cent. of the values in the untreated distillate with no production of light gases or other deleterious changes in the composition of the feed. In most instances the olefin reduction effected by the present process is substantially complete and usually exceeds 90 per cent. Operation of our process with clay-treated feed stocks has been found particularly advantageous in that longer conversion periods between catalyst regenerations are possible than is the case when processing non-clay treated distillates. The beneficial results of our process are reflected in greatly increased octane ratings of treated distillate as measured by the 1-C and 3-C methods in the presence of added tetraethyl lead.

Among the objects of the present invention are to process cracked gasoline distillates of varying degree of unsaturation to produce aviation gasoline blending stocks of at least 50% decreased unsaturation; simultaneously to remove unsaturated hydrocarbons and sulphur so as to increase the lead response of the treated distillates and to pass cracked gasoline distillates over a silica-alumina catalyst in order to prepare high quality aviation gasoline blending stocks.

In accordance with the present invention the process for the improvement of cracked gasoline distillates to effect a reduction in olefin and sulphur content thereof comprises contacting said dis-

tillates with a synthetic silica-alumina catalyst comprising 0.1 to 10 per cent. by weight of hydrous aluminum oxide supported on silica gel under polymerizing conditions of temperature and pressure such that olefin hydrocarbons and sulphur-containing compounds are converted to compounds boiling above the gasoline boiling range and fractionating the effluent from the catalyst zone to eliminate substantial quantities of the original unsaturated hydrocarbons and sulphur compounds in the form of high-boiling conversion products. The distillation characteristics of the final product are substantially the same as those of the original feed stock.

The catalyst utilized in accordance with this invention is a silica-alumina composition and is further characterized, in its preferred form, by the procedure employed in its manufacture. A hydrous silica gel is prepared from an alkali silicate and an acid. The freshly prepared gel, either in a wet or partially dry condition, is treated with an aluminum salt solution such as the chloride or sulphate. The treated gel is then washed free of water-soluble compounds and dried. The alumina, presumably in the form of a hydrous oxide, is selectively adsorbed by the hydrous silica and is not removed by subsequent washing operations. This minor proportion of alumina is from 0.1 to 10 per cent. by weight, and is preferably from 0.1 to 2.0 per cent. by weight. Silica-alumina catalysts prepared by the above procedure possess unique properties particularly suited to the objects of the present invention. Other synthetic silica-alumina catalysts containing from 0.1 to 10 per cent. by weight of alumina and particularly those containing the preferred silica-alumina proportions may be used to treat the materials described herein with desirable but less striking results.

Temperature conditions for the treating operation are selected in accordance with the state of activity of the catalyst. Ordinarily the bromine number of the effluent product is employed as an index of required temperature conditions. With fresh catalyst, product having bromine numbers between 0 and 3 may be derived from olefin-containing stock at temperatures of about 250-300° F. In order to produce a uniform, low bromine-number product, the catalyst temperature is increased incrementally as the catalyst ages. The temperature increase and the point of time at which it is to be made, may be determined experimentally by

determining bromine numbers of snap samples taken as the run progresses. When this number exceeds a predetermined maximum, the temperature may be raised slightly, say 25 degrees. The upper temperature limit is usually fixed at about 600° F. Between these upper and lower temperature limits as much as 1000 volumes of unsaturated distillate per volume of catalyst have been satisfactorily treated without the need of regenerative procedures. Satisfactory reduction of the sulphur content also occurs under the above temperature conditions, and in general, substantial reduction in sulphur and olefin content may be obtained at temperatures between 250—600° F. in accordance with the present invention.

For maximum treating efficiency and long catalyst life, reaction pressures are employed which prevent complete vapourization of the hydrocarbon feed at requisite treating temperatures. We have found that mixed phase and liquid phase treating are equally efficacious with the former having the advantage of being readily operated in conventional refinery equipment by virtue of the relatively low pressure requirements. Depending on the distillation characteristics of the feed stock, pressures of from 200 to 1000 psig may be employed. In mixed phase operation we prefer pressures between about 300 and 500 psig while liquid phase operation is conveniently carried out at about 800 to 1000 psig. Substantially higher pressures may be used; however, no obvious benefits result therefrom. In any event, it is desirable to maintain a substantial proportion of the hydrocarbon undergoing treatment in liquid phase.

Under the preceding conditions of temperature and pressure, when the production of a product of minimum bromine number and sulphur content is desired, treating flow rates may vary between about 0.5 to 5.0 liquid volumes of feed per volume of catalyst per hour with preferred rates in most cases being between about 1 to 3 volumes per hour.

The present treating process is applicable to cracked gasoline distillates con-

taining olefinic and sulphur-containing components and derived from thermal or catalytic processes. With the production of suitable aviation gasoline ingredients, as the criterion of permissible ultimate sulphur and unsaturated hydrocarbon content of treated stocks, the present process may be applied to distillates with bromine numbers as high as 40 to 50 and with sulphur contents up to about 1.0 per cent. by weight. In order to realize the maximum potentialities of our process, we prefer to treat distillates conditioned by prior conventional clay treatment. Such clay treatment is usually carried out by contacting the gasoline distillates being treated with solid adsorbent material such as fuller's earth under such conditions of temperature and pressure that the cracked gasoline being treated is first maintained in the vapour phase. Thus it is not intended that the present catalytic treatment be considered as a substitute for clay treatment inasmuch as the functions of the two processes are distinctly different and complementary.

In further illustration of the specific uses and advantages of the present invention, the following examples are offered.

EXAMPLE I.

A clay-treated catalytically cracked gasoline having a boiling range of 200° to 330° F. was subjected to treatment over silica-alumina catalyst prepared as described above and containing about 1.5% of alumina to effect reduction in olefin and sulphur content. The treatment was carried out under a pressure of 1000 psig at a flow rate of 2 liquid volumes per volume of catalyst per hour while gradually increasing the temperature from 300 to 500° F. The run was discontinued after treatment of approximately 500 volumes of feed per volume of catalyst. The improvement realized from the catalytic retreatment is reflected in the subjoined table where the feed stock and feed stock fractionated so as to give a product having the same boiling range as the catalytically treated and fractionated product are compared as to quality and physical characteristics with the finished product.

	Feed Stock	Fractionated Feed Stock	Catalytically Treated and Fractionated Products
Yield (based on feed), vol. %	—	97.1	96.6
API gravity, 60° F.	39.3	39.0	38.5
Total sulphur, wt. %	0.180	0.160	0.074
Sulphur reduction, wt. %	—	11	59
Bromine number	9	8	4
3-C Blending value	—	—	—
IMEP	191.9	195.4	231.9
S+ml TEL	0.65	0.82	3.15

	ASTM Distillation, °F.	Feed Stock	Fractionated Feed Stock	Catalytically Treated and Fractionated Products
	5%	208	218	218
	10%	219	224	224
5	50%	250	252	254
	90%	303	301	302
	95%	316	314	313

A similar run carried out on a non-clay-treated feed stock showed favourable reduction in sulphur and bromine number during the active life of the catalyst; however, the indicated catalyst life was less than one-half of that found when 15 charging clay-treated stock.

EXAMPLE II.

The clay-treated feed stock of Example I was treated over the silica-alumina catalyst at a flow rate of one liquid 20 volume of feed per volume of catalyst per

hour. The new catalyst was prepared in the same manner as that of Example I but was pretreated with dry nitrogen gas at about 300° F. while the catalyst case temperature during the hydrocarbon 25 treatment was gradually increased from an initial of 225° F. to about 500° F. at the conclusion of the run. As in Example I, the pressure was held at 1000 psig. The beneficial effect of the longer contact time on the quality of the product and the efficiency of treatment is shown in the following tabulation:—

	Feed Stock	Catalytically Treated and Fractionated Products
35	Yield (based on feed), vol. %	87
	Total sulphur, wt. %	0.130
	Sulphur reduction, wt. %	9
	Bromine number	83.0
40	1-C Blending octane number	88.4
	3-C Rich blending value	191.9
	IMEP	250.5
	S+ml TEL	4.83

At the conclusion of this operation the 45 catalyst was still active after treating approximately 500 volumes of feed per volume of catalyst.

EXAMPLE III.

The conversion of a thermally cracked 50 gasoline into a suitable aviation gasoline blending stock by means of treatment over silica-alumina catalyst prepared as described above is illustrated in the operation of this example. The charge to the 55 silica-alumina treatment was a clay-treated gasoline prepared from straight run naphtha under severe thermal (non-

catalytic) cracking conditions. The treatment of this stock was carried out under liquid phase conditions at tempera- 60 tures between 225 and 550° F. and at a pressure of 1000 pounds per square inch. The treatment was started at 225° F. and the reaction temperature was increased in 25° F. increments in order to 65 maintain the desired degree of polymerization. The total treated effluent was fractionated to an end-point of about 350° F. to prepare a finished gasoline base stock. The following data are 70 indicative of the value of the treatment.

	Feed Stock	Catalytically Treated and Fractionated Products
75	Total sulphur, wt. %	0.039
	Bromine number	0.022
	API gravity, 60° F.	3
	3-C Blending value	44.3
	IMEP	180.4
	S+ml TEL	0.29
80	% S in M. (base)	95.8
	ASTM Distillation, °F.	196
	IBP	224
	10%	266
	50%	340
85	90%	391
	EP	348

Although a low-sulphur feed was employed in this test, a sulphur reduction of 43 per cent. was realized. The reduction in bromine number is especially 90

significant, indicating that highly unsaturated stocks can be converted into suitable aviation gasoline stock. The improvement in rich rating from the equivalent of 95.8 per cent. S reference fuel in M reference fuel to a rating of 0.29 ml TEL in S represents the conversion of motor fuel gasoline into an excellent aviation gasoline blending stock.

EXAMPLE IV.

A relatively high fraction of clay-treated catalytically cracked gasoline

was subjected to further treatment over the silica-alumina catalyst prepared as described above under the following conditions: temperature range, 300—400° F.; pressure, 1000 psig; flow-rate, 2 liquid volumes per volume of catalyst per hour. The treated effluent was fractionated to give a stock having approximately the same boiling range as the feed. The subjoined data show that a marginal aviation gasoline stock has been converted into a satisfactory component of high-octane aviation gasoline.

	Feed Stock	Catalytically Treated and Fractionated Products
Total sulphur, wt. %	0.037	0.015
Bromine number	21	1
API gravity, 60° F.	28.9	48.4
1-C Octane number (+4.6 ml TEL)	88.4	91.5
3-C Blending value		
IMEP	205.5	217.3
S+ml TEL	1.37	2.09

EXAMPLE V.

An olefin-rich fraction of gasoline having a true boiling range of 115—200° F. was prepared from clay-treated full range catalytically cracked gasoline. The efficiency of the silica-alumina catalyst prepared as described above in reducing unsaturation and sulphur con-

tent was tested at widely different treating pressure levels, with other conditions remaining substantially the same in both operations. The essential data from these operations are presented in tabular form along with pertinent information on the clay-treated feed stock.

	Feed Stock	Catalytically Treated and Fractionated Products
Operating pressure, psig	—	1000 400
Temperature, °F.	—	300—450 375—450
Feed rate, liq. vol./vol. catalyst/hr.	—	2 2
Yield, vol.% of feed	—	89.4 90.0
API gravity at 60° F.	54.4	54.4 54.4
Total sulphur, wt. %	0.029	0.013 0.010
Sulphur reduction, %	—	55.4 65.5
Bromine number	17	1 1
Bromine number reduction, %	—	94.0 94.0
1-C Octane number (+4.6 ml TEL)	88.4	90.6 90.5
3-C Blending values		
IMEP	198.2	206.4 206.5
S+ml TEL	0.96	1.42 1.43
ASTM Distillation, °F.		
5%	157	160 158
10%	158	160 159
50%	162	164 163
90%	170	172 170
95%	173	178 175

The excellent results obtained at the above pressures indicate that equally good results may be obtained under substantially liquid phase treating as at 1000 psig or mixed phase conditions as prevailing at 400 psig. As shown by the 1-C octane numbers and 3-C rich mixture rating, a marginal blending stock has been converted into a premier grade aviation fuel component which may in turn be blended with marginal stocks to

result in an increased volume of high-grade aviation gasoline.

EXAMPLE VI.

Fractions of catalytically cracked gasoline covering the boiling ranges of 150—160° F., 160—180° F. and 200—350° F. were subjected to treatment over the silica-alumina catalyst prepared as described above without prior conditioning treatment other than fractional dis-

tillation. All test runs were carried out at a pressure of 1000 psig over a temperature range of 350—450° F. and at a flow-rate of 2 liquid volumes per volume of catalyst per hour. The effluent from each

operation was redistilled to eliminate high-boiling, sulphur-containing polymers and to furnish the finished blending stock. Pertinent data are presented in the following tabulation:—

	Gasoline Boiling Range 150°—150° F.		160—180° F.		200—350° F.	
	Feed	Product	Feed	Product	Feed	Product
Yield, vol. % of feed	—	83	—	84	—	97
API gravity, 60° F.	61.6	63.4	41.3	41.0	37.1	36.9
Total sulphur, wt. %	0.059	0.001	0.229	0.127	0.279	0.148
Sulphur reduction, wt. %	—	98.5	—	44.5	—	47.0
Bromine number	47	17	29	13	10	4
Bromine number reduction, %	—	64	—	55	—	60
3—C Blending value	—	—	—	—	—	—
IMEP	135.1	151.7	205.0	251.0	175.9	229.8
S+ml TEL	—	—	1.34	4.89	0.17	2.98
ASTM Distillation, °F.						
5%	152	153	166	167	233	238
10%	153	153	167	168	237	242
50%	155	155	169	170	256	259
90%	158	158	172	172	295	295
95%	160	160	174	174	306	306

The above data clearly indicate that excellent quality improvement can be effected by this treatment on raw effluent from cracking operations. The low quality 150—160° F. fraction is included because of the great improvement realized with respect to bromine number and sulphur content, thereby permitting its inclusion in aviation gasoline as marginal blending stock. More frequent regeneration of catalyst is required when operating with non-clay treated fractions; however, treating costs are still not excessive.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the improvement of cracked gasoline distillates to effect a reduction in olefin and sulphur content thereof which comprises contacting said distillates with a synthetic silica-alumina catalyst comprising 0.1 to 10 per cent. by weight of hydrous aluminum oxide supported on silica gel under polymerizing conditions of temperature and pressure such that olefin hydrocarbons and sulphur-containing compounds are converted to compounds boiling above the gasoline boiling range and fractionating the effluent from the catalyst zone to eliminate substantial quantities of the original unsaturated hydrocarbons and sulphur compounds in the form of high-boiling conversion products.

2. A process according to claim 1,

wherein the contact temperature range is from 250° F. to 600° F. and the pressure is such that at least a portion of said distillates are maintained in liquid phase.

3. A process according to claim 2, wherein the pressure range is from 200 to 1000 pounds per square inch gauge.

4. A process according to any of the preceding claims, wherein the flow rate of the distillates is from 0.5 to 5 liquid volumes per volume of catalyst per hour.

5. A process according to any one of the preceding claims wherein the fractionation eliminates substantially all of the unsaturation and at least a half of the sulphur as high-boiling conversion products.

6. A process according to any one of the preceding claims, wherein the cracked gasoline distillates are first clay-treated prior to contacting with the synthetic silica-alumina catalyst.

7. The processes of treating cracked gasoline distillates substantially as set forth in Examples I—VI.

8. Cracked gasoline distillates whenever treated by a process according to any one of the preceding claims.

Dated the 23rd day of November, 1945.

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